Nanocellulose-Soybean Oil Composites via UV-Initiated Free Radical Polymerization

Katrina B. Hanson[1]
University of Minnesota Twin Cities, Minneapolis, MN 55455
University of Wisconsin River Falls, River Falls, WI 54022

Supervised by

William Tze, Ph.D.[2]
University of Minnesota Twin Cities, Minneapolis, MN 55455

Plant-derived materials are desirable, due to their reduced environmental impact, as an alternative to traditionally petroleum-based materials for a variety of potential applications. Recent work has shown that nanocellulose paper possesses superior characteristics over standard weight paper and that soybean oil can be chemically modified to produce a UV- curable resin. This study examined the use of cost effective ultra-violet (UV) energy to initiate free radical polymerization of acrylated epoxidized soybean oil resin on nanofibrillated cellulose paper substrates. Curing rate, water absorption, and tensile properties were analyzed with variables including reactive diluent molecular weight and paper substrate porosity. Results of selected treatments showed that nanofibrillated cellulose (32% mass fraction in composites) provided 275% and 180% enhancement, respectively, in tensile stiffness and strength of the cured soybean oil resin. On the other hand, the incorporation of resin resulted in a composite with better stiffness retention in wet conditions compared to the nanopaper substrate. Findings from this study suggest that the nanocellulose-resin composites may be useful as a viable material option upon further process modifications.

Keywords— nanocellulose, composite, UV curing, free radical, soybean oil.

[1] Participant of Undergraduate Research Opportunities (UROP) Program, University of Minnesota Twin Cities
[2] Associate Professor, Bioproducts and Biosystems Engineering Department, University of Minnesota Twin Cities

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Nomenclature

AESO = Acrylated epoxidized soybean oil
DPGDA = Dipropylene glycol diacrylate
FTIR = Fourier Transform Infrared Spectroscopy
NFC = Nanofibrillated cellulose
PET = Polyethylene terephthalate
TPGDA = Tripropylene glycol diacrylate

I. Introduction

Cellulose nanomaterials (also known as nanocellulose) are an emerging material with many promising applications. One such application is to improve mechanical properties and/or reduce thermal expansion of polymeric materials without affecting their optical clarity. By adding nanocellulose to a renewable polymer, the above benefits could be realized while keeping the biobased content of the polymer (Ansari *et al*. 2014). One example of such success is the over 10-time enhancement in stiffness and strength of transparent polymers cured (polymerized) from epoxidized soybean oil with the addition of nano-sized (bacterial) cellulose (Retegi *et al.* 2012). Indeed, the reinforced thermoset (polymer that solidifies with heat) competes well with petroleum-based, commercially available epoxy polymers.

Inspired by the promising properties of nanocellulose-soybean oil composites, this study was aimed at gaining a better understanding of the polymerization (curing) of the oil with plant-based nanocellulose blended in it. To make the curing process more environmentally friendly, ultra-violet (UV) energy was used as a means to reduce the time (and energy) otherwise needed in conventional heat curing (Chen *et al*. 2011). This approach required acrylated epoxidized soybean oil (AESO) (Figure 1), which is commercially available. The acrylate pendant groups were introduced to the chemical structure of the soybean oil in order to activate it for UV curing.

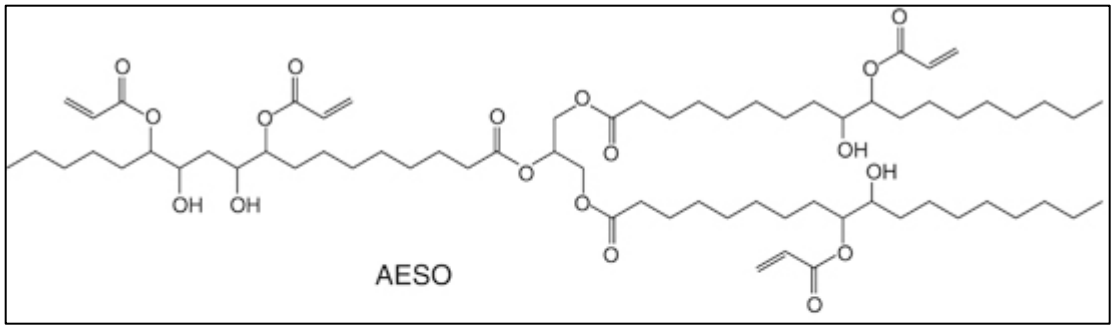

Figure 1. Acrylated epoxidized soybean oil (AESO). Source: Shibata et al. 2011.

A major challenge remains however in blending nanocellulose with most polymeric materials in a non-aqueous condition. Nanocellulose is more inclined to agglomerate to one another than to disperse into the polymer. One way to address this issue is to pre-form nanocellulose mats for infusion of polymer precursors (Rebouillat and Pla. 2013). Most vegetable oil including soybean oil, however, is relatively high in viscosity to allow ease of infusion. Therefore, this study also examined the use of reactive diluents, which not only dilute the functionalized soybean oil, but also cross-link with functionalized soybean oil during the UV curing process. Two diluents, DPGDA (Figure 2) and TPGDA (Figure 3), were chosen for their similar molecular structure and slightly different molecular weight.

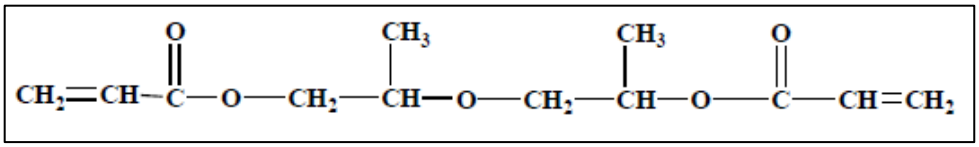

Figure 2. Dipropylene glycol diacrylate (DPGDA).

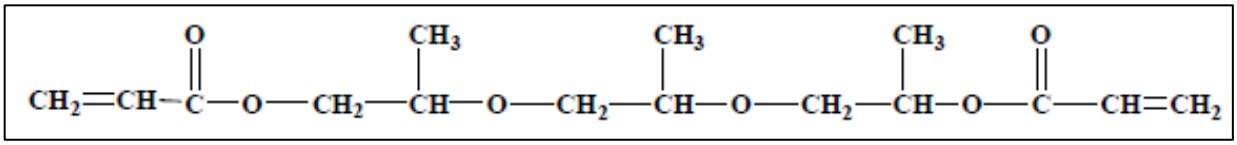

Figure 3. Tripropylene glycol diacrylate (TPGDA).

Summarizing the above elaborations, the specific objectives of this study were to examine:

1) Effects of UV irradiation time on polymerization of acrylated epoxidized soybean oil (AESO);
2) Impacts of nanocellulose on tensile properties of the AESO composites;
3) Effects of cured resin on the wet performance of NFC paper composites;
4) Influence of diluent chain length on the tensile properties of the cured composites.

II. Experimental

A. Materials

The acrylated epoxidized soybean oil (AESO) and 1-hydroxycyclohexyl phenyl ketone (as photoinitiator; Fig. 4) were purchased from Sigma Aldrich (St. Louis, MO). Tripropylene glycol diacrylate (TPGDA) and dipropylene glycol diacrylate (DPGDA) were ordered from TCI America (Portland, OR). All reagents were used without further purification.

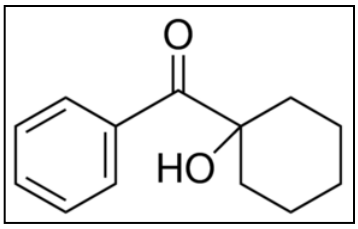

Figure 4. 1-hydroxycyclohexyl phenyl ketone as photoinitiator.

The nanocellulose used for the composites were prepared in the lab from bleached Kraft hardwood pulp via ultra-fine friction grinding in water followed by vacuum filtration of the resulted nanofibrillated cellulose (NFC) suspension. Two types of NFC paper substrates were produced: regular (vacuum filtration from water) and of increased porosity (vacuum filtration from pre-adjusted 1:1 v/v water-ethanol mixture).

Prior to making composite specimens, NFC paper substrates were placed between absorbent blotter sheets and weighted on top with four ring masses (total ~1.2 kg) in a 100 °C oven for at least four hours to achieve an oven dry state. The oven-dried substrates were cut into 1" x 3" strips which were individually weighed, sealed in zipper bags, and stored in a desiccator until ready to use.

B. Preparation of Composite Specimens

The resin was prepared by adding AESO (9.0 g), DPGDA or TPGDA (3.0 g), and photoinitiator (0.6 g) to a small beaker followed by stirring with a magnetic stir bar at 200 rpm and 60 °C for 20 minutes. An amount of resin equivalent to 1.5x the mass of paper substrate was applied to each side of the 1" x 3" substrate. The resin-applied substrate was sandwiched between two mil-thick PET liners (also 1" x 3" in size) pre-cleaned with acetone. Air bubbles trapped between the liners were removed by gently pushing them to the edges with fingertips. The specimens were cured between 0 and 60 seconds with UVA (320-390 nm wavelength) using a DYMAX 5000-EC UV curing flood lamp system at an irradiation intensity of 150 mW/cm^2. At the end of target UV exposure time, tweezers were used to remove the PET liners from the specimens which were then weighed, placed in individual bags, and stored in a desiccator prior to testing. A similar procedure was performed to prepare resin films (without NFC), in which case 0.4 g of resin was placed directly between the PET liners.

C. Material Characterization

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR analyses were performed using Nicolet Series II Magna-IR System in attenuated total reflectance (ATR) mode. A drop of the resin (including diluent and initiator) was placed on the ATR crystal for spectra collection at a resolution of 4 cm^{-1} and accumulation of 32 scans. The absorption band at ~1640 cm^{-1} corresponding to the C=C stretching of vinyl group (Åkesson *et al.* 2010) was examined, and its intensity was normalized (divided) by the band intensity value of methyl group (1376 cm^{-1}; CH_3 from diluent) which did not participate in resin polymerization. A degree of conversion (χ) was calculated from the normalized intensities (I) before UV irradiation (t=0) and upon irradiation for a period of time t (Sideridou et al. 2002):

$$\chi = \left(\frac{I_0 - I_t}{I_0} \right) 100\%$$

Tensile Testing

The 1.5" x 3" strips after curing were die-cut to 0.375" x 2.5". For samples that were to be wet-tested, two tensile specimens were cut from each strip, so that one could be tested dry as the reference. If only dry testing was to be performed, one test specimen was cut from each strip. Prior to testing, all test specimens were placed in a 50% relative humidity room for 72 hours for conditioning. The conditioned specimens were measured at three locations for thickness using a motor-driven micrometer (manufactured by AB Lorentzen & Wettre, Stockholm) equipped with a Mitutoyo Digimatic Indicator. They were then tested to failure in tension mode at an initial gauge length of one inch and loading rate of 0.2 in/min using an INSTRON 5542 fitted with a 500-N load cell. Young's modulus, maximum stress, and strain at break were calculated from the load-displacement data.

After tensile testing, the specimens were placed in the oven to dry at 100 °C until constant mass. Moisture content and specific gravity of the specimens at the time of tensile tests were then calculated. Moisture content refers to the mass of moisture relative to the overall mass of the specimens. Specific gravity refers to oven-dried mass of the specimen divided by its volume at test conditions, and it is expressed relative to the density of water.

Water Absorption

Specimens (0.375" x 2.5") were soaked in deionized water for 24 hours. Jars with a diameter of less than 2" were used to keep the specimens from floating on the surface of the water. This encouraged uniform water absorption over the entire surface area of the specimens. The mass and thicknesses of the specimens before and after soaking were measured to calculate water absorption and thickness swelling relative to (divided by) the initial mass or thickness. The specimens were then tested (without conditioning) via the tensile testing procedure above following the same method as the dry specimens.

III. Results and Discussion

A. Effect of UV Exposure on the Curing of Soybean Oil Resin

Upon UV exposure, the band at 1637 cm^{-1} (C=C bond) reduced in intensity (Figure 5), indicating cleavage of C=C bonds for free radical polymerization of the resin. The band disappeared after 10 seconds of UV exposure, suggesting that complete polymerization had occurred. This is further indicated by the graph in Figure 6, which shows a complete (100%) conversion from double bond to single bond within a UV exposure time of 10 seconds for either type of diluent mixtures. To avoid surface tackiness, 50 seconds was established as the curing time for subsequent studies.

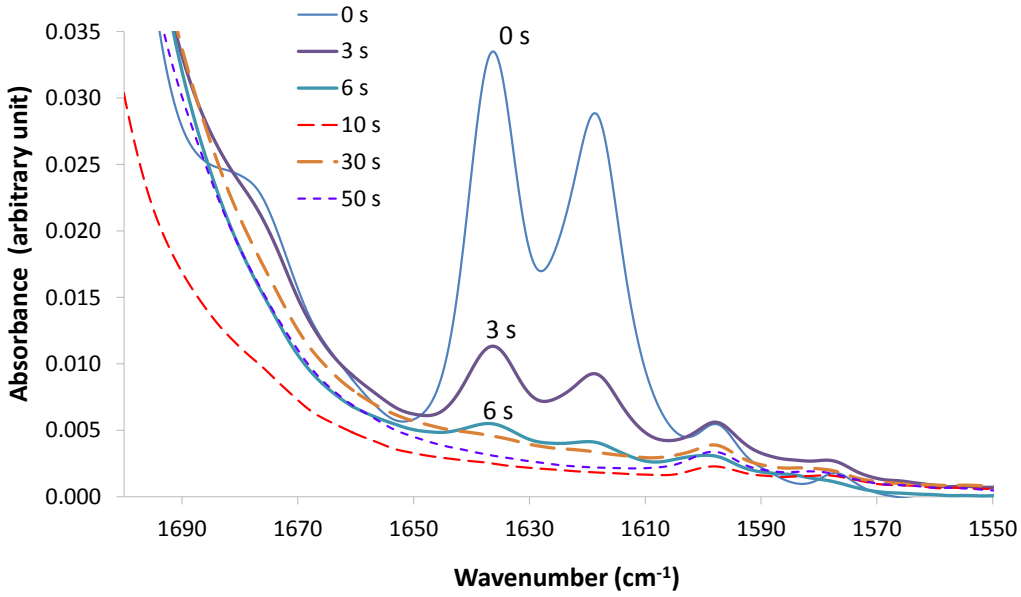

Figure 5. FTIR spectra indicating the disappearance of the C=C bond upon curing of rein (DPGDA diluent).

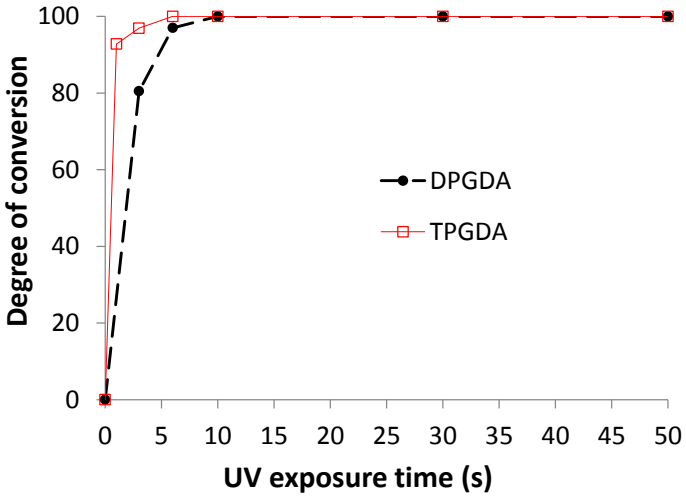

Figure 6. Degree of conversion as the resin mixture (without paper) was exposure to UV irradiation.

B. Reinforcement Effects of Nanocellulose in Soybean Oil Resin

The composites contained ~68 wt% of cured resin as calculated from mass increase after resin incorporation and curing. Figure 7 shows that at a mass fraction of 32%, the nanofibrillated cellulose (NFC) resulted in a 275% increase in tensile modulus and 180% increase in strength of soybean oil resin (cured for 50 s). This reinforcement took place without compromising ductility, as evidenced by the strain at break, which remained similar (See Figure 7).

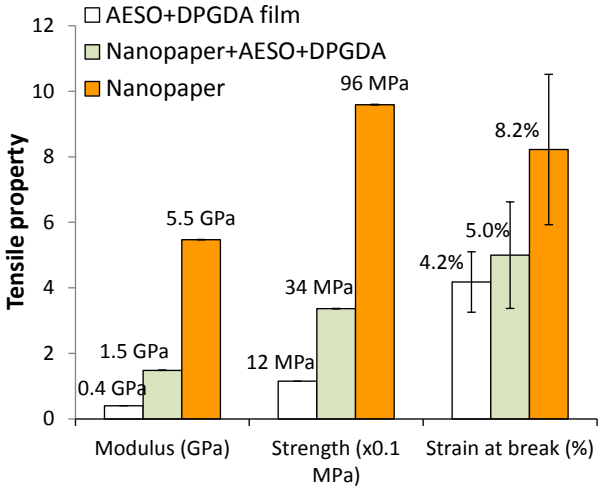

Figure 7. Tensile properties of conditioned samples

C. Effects of Resin on Wet Performance

Water absorption studies revealed that soaked paper-resin composites were lower in moisture content compared to soaked NFC paper, and the difference is attributed to the high water resistance of the cured resin (Figure 8). With resin incorporated and cured, the water absorption (uptake) was reduced from 104% (NFC paper) to 22%. Thickness swelling was also reduced from 92% to 19%, which corresponds to the reduction in water uptake for the composite specimens.

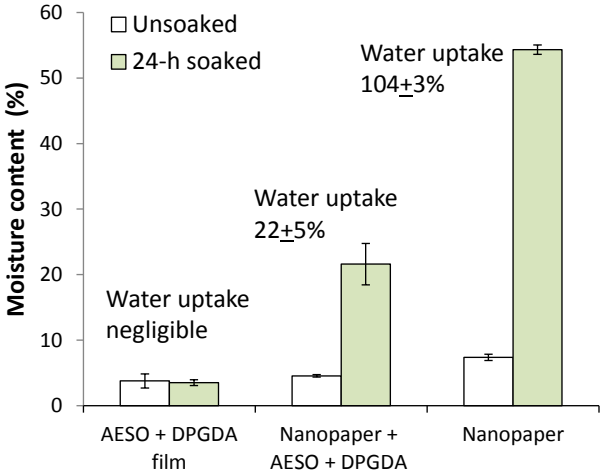

Figure 8. Moisture content and water absorption of soaked samples.

In wet conditions, tensile stiffness was better retained in (cured) resin-containing samples. The modulus of NFC paper-resin composites was measured to be 250 MPa, versus 70 MPa for NFC paper (Figure 9). On the contrary, the wet strength and ductility were higher in paper substrates than composites. This result can be related to the observed delamination between the resin and paper substrates upon soaking. The delamination could be remedied by improving cellulose-resin compatibility, which would need to be addressed in further studies. Overall, certain wet performance characteristics are improved by adding resin to the nanocellulose paper, while more profoundly, nanocellulose benefits the resin film in dry condition (as discussed for Figure 7).

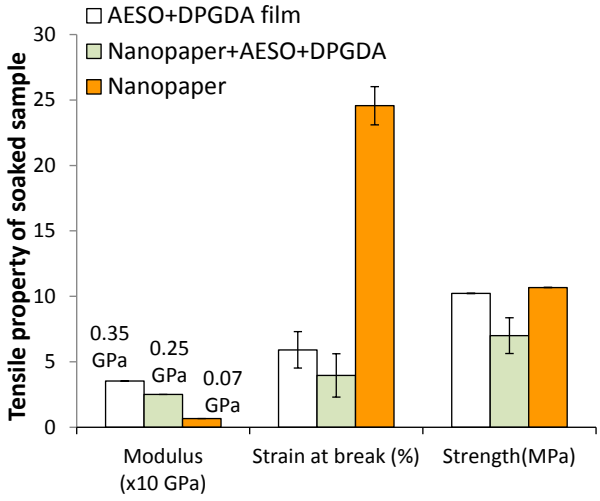

Figure 9. Tensile properties of soaked samples.

C. Effects of Substrate Porosity on Tensile Properties of the Resin Composites

The results discussed so far pertain to (regular) nanopaper formed from water. In this section, nanopaper formed from ethanol solution was also examined to discern the effect of porosity. This latter substrate was approximately 20% lower in density than the paper formed from water (Figure 10). A lower density indicates higher paper porosity, and it is due to larger fibril-to-fibril distances as a result of lower capillary force (lower surface tension of ethanol) during mat formation. Capillary force is responsible in pulling fibers (or fibrils) together in regular paper formation.

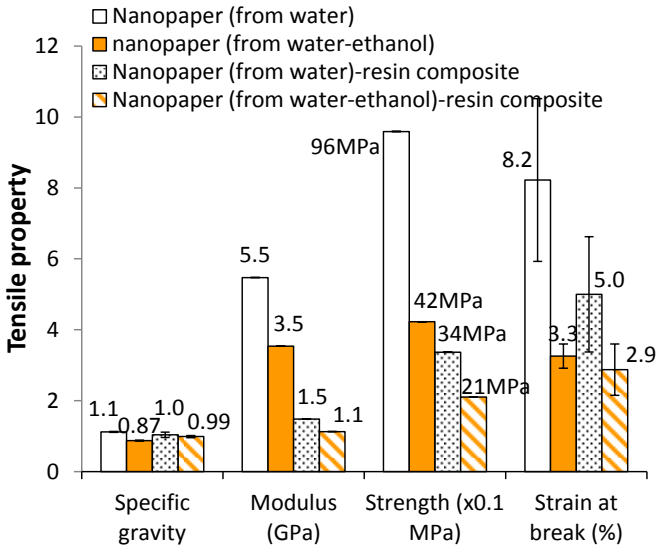

Figure 10. Tensile properties of AESO+DPGDA film and composite samples from two different nanopaper.

The more porous nanopaper had a lower degree of interfibril bonding, thus it was lower in modulus (by 35%), strength (by 55%), and strain at break (by 60%) compared to regular nanopaper (Figure 10). When combined with soy bean oil resin with DPGDA as the diluent, the resulted composite was also lower in stiffness, strength, and ductility compared to resin composites of regular nanopaper. These lower properties were likely due to the lower degree of fibril network percolation within the cured resin. Here, it is worth pointing out that the two types of nanopaper were originally intended to examine effects of differing resin infusion into the paper substrates, but the resin loading hence fraction in the prepared composite was too high for the purpose.

D. Effects of Diluent Chain Length on Tensile Properties of the Cured Resin Film and Composites

Two reactive diluents of different chain length were used in soybean oil resin formulations. Referring back to Figures 2 and 3, TPGDA has three propoxys [$CH_2CH(CH_3)O$] in the molecular chain backbone while DPGDA has two propoxys. This difference accounts for improved ductility of the resin film formulated with TPGDA, as indicated by a 50% higher strain at break (Figure 11). Ductility was also 60% higher for the nanopaper (formed in water) composite of TPGDA resin formulation. Tensile modulus and strength, however, were affected little to none by the type of reactive diluent used. This is a reasonable result if it is assumed that the vinyl groups at both ends of the diluent molecule provide sites for crosslinking with the resin; the longer chain length between crosslinks leads to higher ductility of the cured resin.

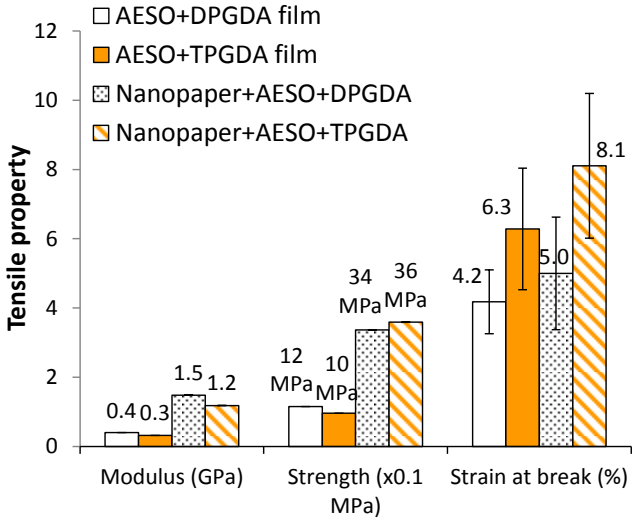

Figure 11. Tensile properties of resin film and composite samples containing either DPGDA or TPGDA diluent.

IV. Conclusion

This study examined the ability of acrylated epoxidized soybean oil resin to form a composite with pre-formed nanocellulose web substrates. Two types of NFC paper and two reactive diluents were included in the experimental design to determine the possibility of such a composite to increase its performance characteristics over the materials individually. FTIR results indicated that ultraviolet irradiation was a successful curing method, which was visually supported by the solidification of the resin. The addition of resin reduced water uptake of the resulted composites and improved preservation of their wet stiffness. Diluent with the higher molecular weight resulted in resin films and composites with higher ductility (strain at break). Additionally, nanopaper created with higher porosity formed resin composites that exhibited a lower modulus, strength, and ductility than the lower porosity version.

The experimental results suggest that UV cured NFC paper incorporated with soybean oil resin could hold promise for the future of plant-based composite materials. Additional studies should be performed to determine optimal resin formulation and dosage. These factors have the potential to reduce specimen tackiness and surface resin transfer and hopefully allow for a reduced curing time. Other coating methods could be explored to more closely control resin thickness. With these modifications as well as others as required, there is evidence that NFC-soybean oil resin composites could be a useful and cost-effective environmentally friendly material.

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